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Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 5:

Cancer Chemotherapy to Ceramic Colorants

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Production Director: Maximilian Montkowski
Production Manager: Myriam Nothacker

Library of Congress Card No. 84-25-829

Deutsche Bibliothek, Cataloguing-in-Publication Data:

Ullmann's encyclopedia of industrial chemistry / executive ed.: Wolfgang Gerhartz. Senior ed.: Y. Stephen Yamamoto. Ed.: F. Thomas Campbell ... [Ed. advisory board Hans-Jürgen Arpe ...]. — Weinheim ; New York, NY : VCH

Bis 4. Aufl. u. d. T.: Ullmann's Enzyklopädie der technischen Chemie

NE: Gerhartz, Wolfgang [Hrsg.]; Encyclopedia of industrial chemistry

Vol. A. Alphabetically arranged articles.

5. Cancer chemotherapy to ceramic colorants. -- 5th, completely rev. ed. 1986.

ISBN 3-527-20105-X (Weinheim)

ISBN 0-89573-155-X (New York)

© VCH Verlagsgesellschaft mbH, D-6940 Weinheim (Federal Republic of Germany), 1986.

Distribution: VCH Verlagsgesellschaft, P.O. Box 12 60/12 80, D-6940 Weinheim (Federal Republic of Germany)

USA and Canada: VCH Publishers, Suite 909, 220 East 23rd Street, New York NY 10010 (USA)

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Cover design: Wolfgang Schmidt

Composition, printing, and bookbinding: Graphischer Betrieb Konrad Triltsch, D-8700 Würzburg
Printed in the Federal Republic of Germany

and glucose to fructose using α -amylase, glucoamylase, and glucose isomerase; and the hydrolysis of proteins and peptides by various proteases in detergent additives, meat tenderizers, and digestive aids (\rightarrow Enzymes, \rightarrow Immobilized Biomaterials).

5. Production of Catalysts

Because *homogeneous catalysts* are mostly well-defined chemical compounds or complexes, their catalytic performance does not depend on the preparation method. On the other hand, the catalytic properties of *heterogeneous catalysts* are strongly affected by every step of the preparation. Therefore, producing a catalyst reproducibly requires that the production steps and operating conditions are accurately defined and carefully controlled. There is also a need for strict quality control of the raw materials used in the preparation because even trace impurities can often modify catalytic performance.

5.1. Supported and Unsupported Catalysts

With many catalysts, the major component is the active material. Examples of such *unsupported catalysts* are the silica-alumina and zeolites used for cracking petroleum fractions and the Pt-Rh gauze used for oxidation of NH_3 to NO.

In numerous other catalysts, the active material is the minor component, which is deposited on a more or less inert porous *support* (carrier). The support primarily serves to disperse the active component over a large surface area and to provide the needed mechanical form and strength. Examples of supported catalysts are activated-carbon-supported Pt and Pd, and Ni on alumina.

5.2. Supports

During the first few decades of this century, catalyst supports were derived from such *natural high-surface-area materials* as pumice, kieselguhr, asbestos, kaolin, and bauxite. Currently, many *synthetic supports* are available in a wide

range of surface areas, porosities, shapes, sizes, and purities. The widely used supports include aluminas, silica gel, activated carbon, zeolites, silicon carbide, titania, magnesia, and various silicates. In addition to the finished formed supports, such precursors as various hydrated aluminas (α - or β -alumina trihydrates, α -alumina monohydrate) and colloidal silicas are also available [203]. The production methods and properties of these materials are described in this encyclopedia under the individual keywords.

Supports with high surface area are as a rule *microporous*. Heat treatment increases pore size, crystallinity, and chemical inertness, whereas surface area and pore volume decrease. The pore size distribution usually has a maximum corresponding to a monomodal distribution. Increased pore volumes of oxide-type supports can be obtained by calcination of special hydrated oxides or hydroxides. For example, high-surface γ -alumina can be obtained by the gradual calcination of α -alumina trihydrate.

The incorporation of volatile or combustible materials (wax, textile fibers, foamed plastics) into the gel form by kneading causes, on calcination, the development of large pores and a pore size distribution that shows two or more maxima. Supports with such bi- or multimodal distribution are useful in reactions in which the selectivity is adversely affected by slow pore diffusion.

In some instances performance of the supported catalyst depends on a *synergistic interaction* between the active component and the support. Such effects are observed in the chromia-alumina and cobalt molybdate-alumina systems. In other cases interaction between the support and the metal or metal oxide deposited on it can strikingly alter the catalytic and chemical properties of the active material. This so-called strong metal-support interaction (SMSI) decreases the chemisorbing ability of titania-supported platinum group metals for H_2 and CO [233]. In addition, SMSI hinders reduction of silica-supported iron oxide and of alumina-supported tungsten oxide [234]. The suppression of H_2 chemisorption of Ni has been observed on silicon carbide and silica supports and has been ascribed to formation of a Ni-Si alloy [235].

Low-surface-area ($< 1 \text{ m}^2/\text{g}$) and low-porosity ($< 0.2 \text{ cm}^3/\text{g}$) supports are generally inert and are available in the form of powders, spheres, cylinders, and granules. They are used with catalysts for selective oxidation reactions

of nitric acid (a film-type binder) in the forming of hydrated alumina, and the use of a calcium aluminate cement (a matrix-type binder), which sets up in the presence of CO_2 and H_2O .

Lubricants are added to improve flow characteristics of the material to be formed, i.e., to reduce friction between the particles and formed aggregates. For this purpose film-type binders and other liquids are used. Solid lubricants are materials with a layer lattice (graphite, talcum powder) or low melting point (paraffin wax, stearic acid) and are used in tableting.

Conventional *supports* (alumina, silica gel) are available commercially in various forms and sizes.

Catalysts are formed by a variety of methods depending on the rheology of the material [238]. Catalysts prepared by precipitation or compounding can be formed before or after washing and drying. *Granules* are produced by grinding and screening. *Microspherical particles* are obtained by spray drying of a solution or slurry. This method is used to produce essentially all fluid-cracking catalysts (0.05–0.25 mm).

The production of *spherical gel-type catalyst* of uniform size involves injection of droplets of a liquid into oil just after the addition of the precipitation agent. Thus, silica gel spheres form from a mixture of nitric acid and an aqueous solution of sodium silicate. The beads descend in a column of oil and are removed at the bottom for aging and subsequent careful washing.

Spherical catalysts can also be prepared on a tilted rotating pan into which the catalyst powder containing a binder is fed. The angle of the tilt and the speed of rotation regulate the size of the spheres formed. Other methods for forming spherical particles include tumbling short extruded cylinders in a rotating drum and also briquetting. In the latter technique, powder and binders are fed between two rotating rolls, the surfaces of which are provided with matching hollowed-out hemispheres.

A common form of catalysts is the *cylindrical pellet*, produced either by extrusion or by tableting. Extrusion produces low-density, high-porosity pellets containing superficial macropores. Extruded pellets down to 1 mm diameter are obtainable from pastes of fine powders or gels by using either ring-roll or auger-type extruders. In the ring-roll method, the mix is fed to a rotating cylinder drilled with numerous holes of a given size. Inside the cylinder one or more compression rolls press the mix through the

holes while on the outside of the cylinder a knife removes the extrudate. In the auger extruder a screw presses a perforated die through the mix and a rotating knife cuts off the extrudate to form pellets.

Tableting produces strong pellets suitable for charging tall reactors requiring particles of high mechanical strength. To ensure uniform filling of the dies in the tableting machine, the feed must be a dry, fine material of good flow characteristics. Irregularly shaped particles, dusty powders, and crystalline materials are hard to tablet. To ensure good flow, only solid lubricants are used in tableting. Tablet sizes below 3 mm are not practical because of high cost and difficulties connected with filling small dies uniformly. Tableted catalysts are unsuitable for reactions in which diffusion limitation affects selectivity because the surface layers of the tablets are strongly compressed and almost exclusively contain micropores.

6. Characterization of Catalysts

Catalysis research uses many physical and chemical methods to characterize catalysts and to search for correlations between the structure and performance of catalysts. These methods include classical procedures [250], [251] as well as techniques developed more recently to study the chemistry and physics of surfaces [252].

6.1. Physical Properties [69]

The *specific surface area* of a catalyst or support (in m^2/g) is determined by measuring the volume of gas, usually N_2 , needed to provide a monomolecular layer according to the Brunauer–Emmett–Teller (BET) method. The specific surface area of active metals dispersed on a support is determined by *chemisorption* of H_2 , CO , NO , or N_2O at or above room temperature [208]. This method gives the number of exposed metal atoms per gram of catalyst and thus the *degree of dispersion*. Knowledge of the degree of dispersion permits comparison of catalytic activity of different catalysts on the basis of rates per unit of metal surface area. To a limited extent the chemisorption technique is applicable to oxides.

The *specific pore volume*, *pore size*, and *pore size distribution* of microporous materials (pore